

GENESIS TUTORIALS

Institute for CSIR-UGC-NET/JRF, GATE & IIT-JAM

Co-ordination Chemistry

The branch of inorganic chemistry that deals with the study of co-ordination compounds is called co-ordination chemistry

A compound in which a metal cation or atom is attached to a group of ligands by co-ordinate bonds is called a co-ordination compounds or complex

Ligands:- Any species (ion or molecule) that have atleast one lone pair or e^- and can donate its lp. of e^- to metal cation or atom is called ligand

It is electron rich species i.e. why it is also called lewis base or Nucleophile

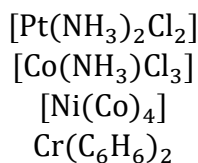
Metal cation:- it is an e^- deficient species which can accept a apir of e^- therefore it behaves as lewis acid or an electrophile

Now, when a group of ligands donotes its pairs of e^- (one pairs by one donor atom of a ligand) to the metal cation or atom co-ordinate bonds are formed and the product so formed is called co-ordination compound.

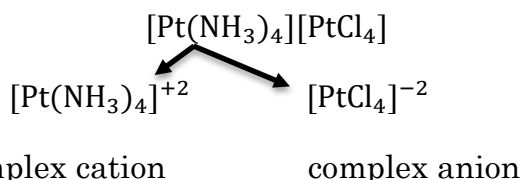
Or, a compound in which a metal cation or atom is attached to a group of ligands by co-ordinate bonds is called Co-ordination compound or complex compound

These can be either neutral or ionic compounds

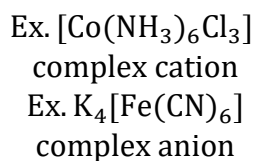
Neutral co-ordinate compound



Ex.



ionic → either the cation or anion or both may be complex ions

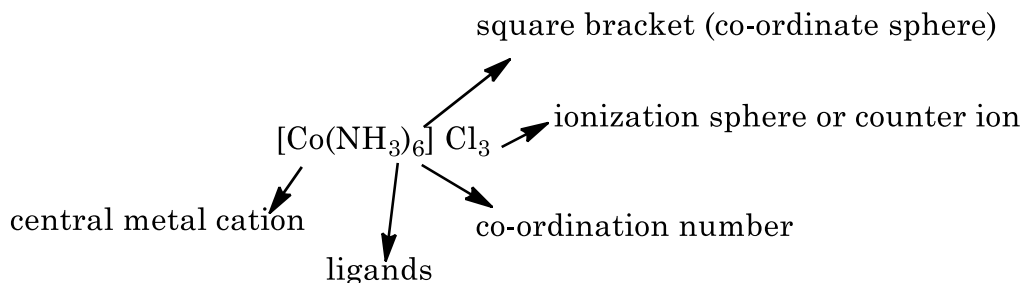


* The co-ordination compounds retain their identity, more or less reaction in solution though partial dissociation may occur.

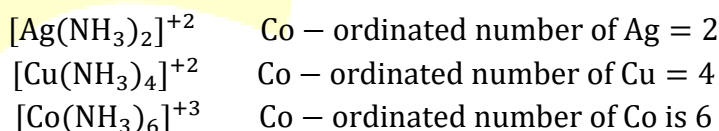
These compounds do not give the tests of all their constituents ions in aqueous solution ie. some constituents ions lost their individual identities in aq. Solution

Ex. $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ is a complex compound and it does not give the test of all the constituent ions because it dissociates as $[\text{Co}(\text{NH}_3)_6]^{+3}$ complex ion and Cl^- ions

Complex ion:- is an ion in which a metal cation is attached to ligand by co-ordinate bonds

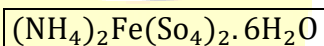


Co-ordination number:- The atom in a ligand that is directly attached to the metal cation or atom is called donor atom and the number of donor atoms attached to metal cation or atom is called coordinated number.

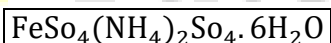


Note:- Double salts:- These compounds lose their identity in solution. These compounds are stable in the solid state but give their constituent ions when dissolved in water or in any other ionic solvent.

Ex. Mohr's salt:- Ammonium iron (II) sulphate



Ex carnallite:- $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$



(1) WERNER THEORY:- Werner proposed a theory of co-ordination compound to explain the structure and formation of compounds 'Werner' was the first inorganic chemistry to be awarded the Nobel chemistry in 1913.

* Werner postulated that metal exhibit two type of valences

- (a) Primary valency (b) secondary valency

In modern terminology, primary valency corresponds to the oxidation number and secondary valency to co-ordination number of metal

Classification of Ligand

Ligands can be classified as monodentate or polydentate ligand (ex. bidentate, tridentate...) depending upon the number of ligand donor atoms that attach to the metal ion or atom

(a) Monodentate ligands:- A ligand which shares e^- pair of a single donor atom with a metal atom or ion is called monodentate ligand.

Negative ligands

F^-	fluoro
Cl^-	chloro
Br^-	bromo
I^-	iodo
OH^-	Hydroxo
O^{2-}	oxo
O_2^{2-}	peroxo
O_2^-	superoxo
H^-	hydrido
CH_3COO^-	acetato
CO_3^{2-}	carbonate
SO_4^{2-}	sulphanato
S^{2-}	sulphido
NH_2^-	amido
NH^-	inido
N^{3-}	nitrido
N_3^-	azido
NO_2^-	nitro (or nitrito – N)
ONO^-	nitrito (or nitrito – O)
SCN^-	thiocyanato (or thiocyanato – S)
NCS^-	isothiocyanato (or thiocyanato – N)
$-CNO^-$	cyanate
$-ClO_3^-$	chlorato

Neutral Ligands

$(C_6H_5)_3P$ triphenyl phosphine

$(C_2H_5)_3P$ triethyl phosphine

C_2H_4 ethylene

$(C_6H_5)_3\ddot{N}$ pyridine (N)

$\ddot{N}H_2 - \ddot{N}H_2$ hydrazine

$CH_3\ddot{N}H_2$ Methyl amine

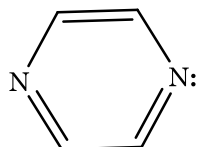
$(\text{CH}_3)_2\text{NH}$ dimethylamine

$(\text{CH}_3)_3\text{N}$ trimethylamine

CH_3CN methyl cyanide or acetonitrile

CH_3NC methyl isocyanide

$\text{C}_2\text{H}_5\text{O C}_2\text{H}_5$ diethyl ether



pyrazine (heterocyclic aromatic organic compound)

NH_2OH

hydroxylamine

Neutral ligands which are given special names

Co carbonyl

NH_3 ammine

Cs thiocarbonyl

H_2O aqua

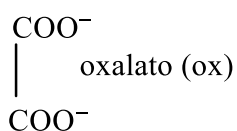
No nitrosyl

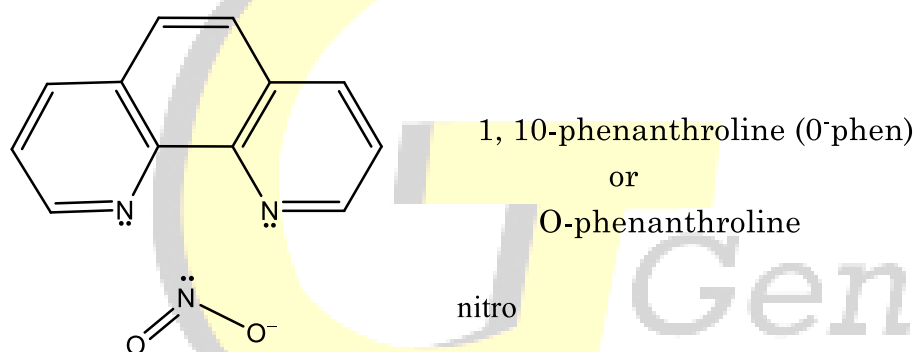
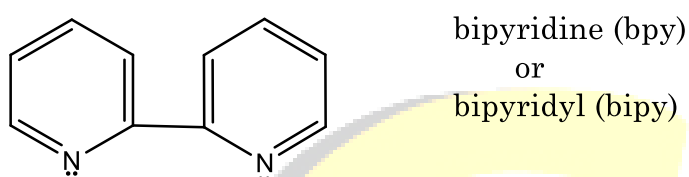
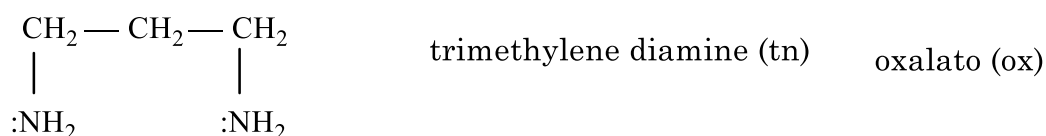
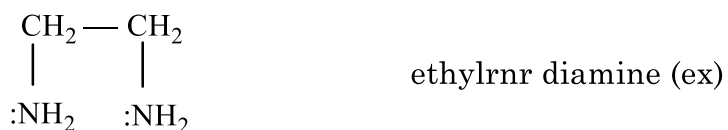
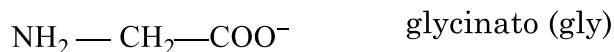
Ns thionitrosyl

* Polydentate ligands or multidentate ligands

→ Ligands that bond to metal cation or atom through e^- pairs present on more than one donor atom are called multidentate ligands. They are also called chelating ligands (because they form one or more rings)

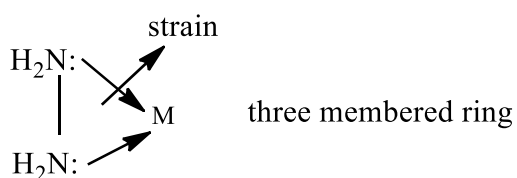
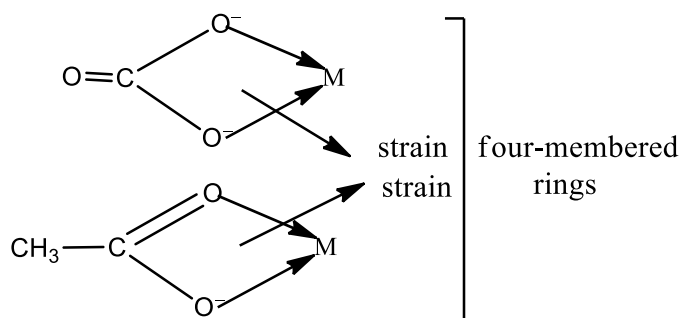
(a) Bidentate Ligands





Note:- The ligand like Co_3^{-2} , CH_3COO^- , NO_2^- , NO_3^- (nitrate ion), SO_3^{-2} , SO_4^{-2} , $\text{NH}_2 - \text{NH}_2$, O_2 , N_2 etc, have two donor atoms, but they act as monodentate ligands.

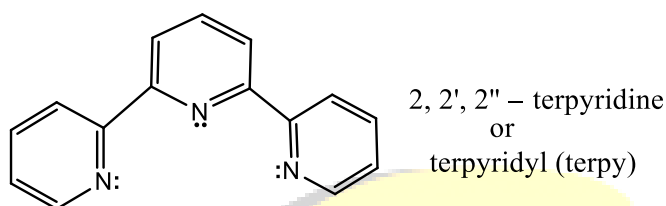
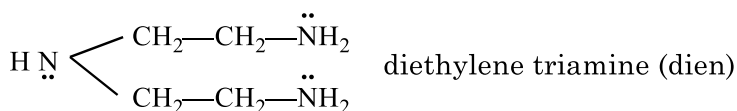
* They form either four or three membered rings including metal cation or atom and there will be repulsion between donor atoms and their e^- pairs which causes the ring to be strained and hence unstable



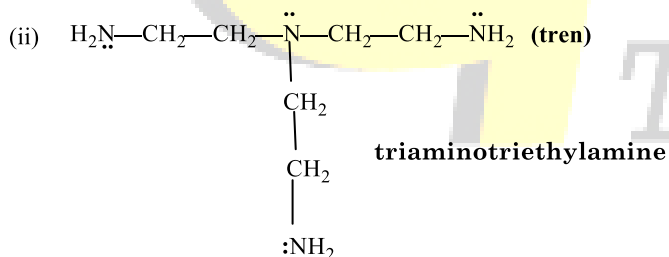
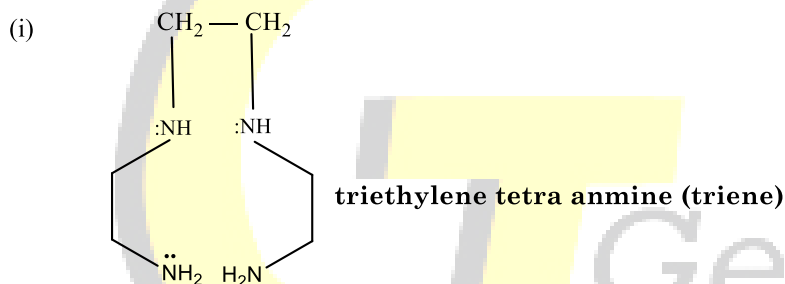
Note:- These ligands may behave as bidentate ligands when the size of metal cation is large like in lanthanoids

Ex. $[\text{Ce}(\text{NO}_3)_6]^{-2}$ in which co-ordination number of Ce^{+4} is 12

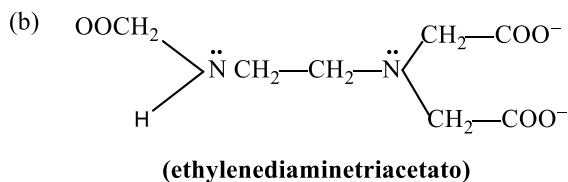
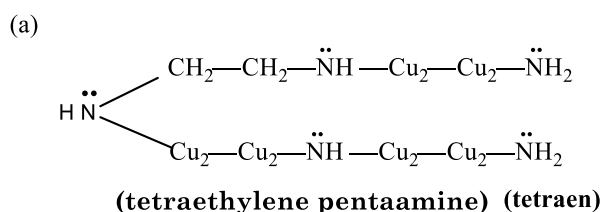
(2) Tridentate ligands:- (Donor atoms are present)



(3) Tetradentate ligands:-

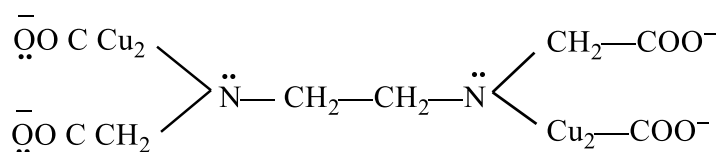


(4) Pentadentate ligands:-



(5) Hexadentate ligands:- edta or EDTA (ethylenediaminetetraacetato)

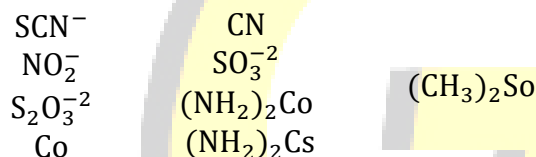
(EDTA⁻⁴) → has 6 donor atoms



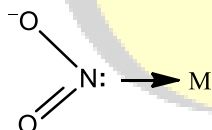
* **Ambidentate Ligands**:- The monodentate ligands which have two or more different donor atoms can co-ordinate to a metal cation through either of two different atoms, these ligands are called Ambidentate Ligands

* When an ambidentate ligands Co-ordinates to the metal cation through either of the two donor atom, two different compound are obtained which are called linkage isomers

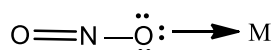
Ex.



Ex.



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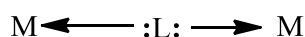


Ex. $\text{M} \leftarrow \text{SCN}^-$

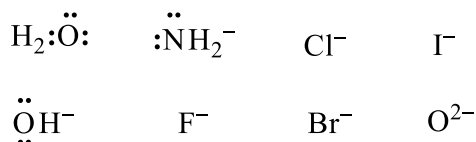
$\text{M} \leftarrow \text{NCS}^-$

Bridging Ligands:- The ligands in which one or two different donor atoms have atleast two pairs of e⁻ and share these e⁻ pairs with two metal ions or atoms simultaneously are called bridging ligands

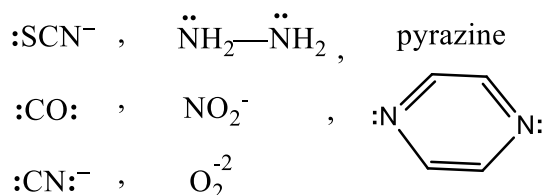
Their interaction with metal ions or atoms can be represented as:



⇒ The monodentate ligands having two lone pair of e⁻ on one donor atom which acts as bridging ligands are

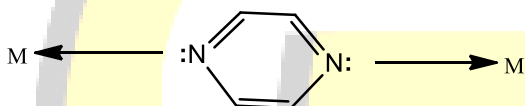


⇒ The monodentate Ligands having two lone pair on two different atoms (one lp on one atom) are



⇒ A bridging ligand forms two σ -bonds with two metal ions or atoms (one σ bond with one metal ion or atom) and these complexes are called bridging complexes or multinuclear or polynuclear complexes

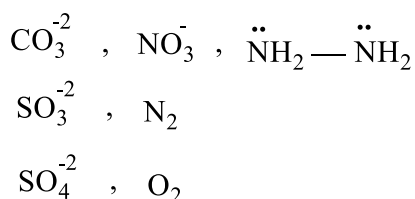
Ex.



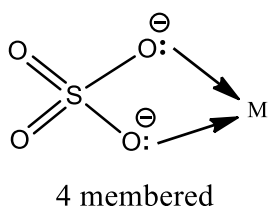
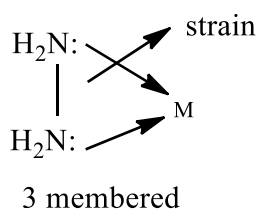
Flexidentate ligands:-

The ligands which have two or more donor atoms can co-ordinate with metal atom or ion either through one donor atoms forming non-chelated complex or two donor atoms forming a chelate these ligands are called flexi dentate ligands

Ex.



* When these ligands behave as monodentate ligands, the complexes so formed are really stable, but when these ligands behave as bidentate ligands, they form chelates containing 3 or 4 membered rings including metal ion.



In general chelates having 3 or 4 membered rings are: unstable because of steric strain. But exceptionally these are some stable chelates having 4 membered rings like.



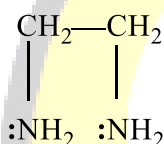
Note:- EDTA^{4-} is a hexadentate ligands, but sometimes it acts as a Pentadentate or tetradentate ligand depending upon the size and stereochemistry of chelate formed.

Ex. In complexes $[\text{Cr}(\text{OH})(\text{HEDTA})]^{-2}$ and $[\text{CoBr}(\text{HEDTA})]^{-2}$, it act as pentadentate ligand and in complexes $[\text{Pd}(\text{H}_2\text{EDTA})]^\circ$ it acts as tetradentate ligands & in complexes $[\text{Ca}(\text{EDTA})]^{-2}$ or $[\text{Mg}(\text{EDTA})]^{-2}$ it act as hexadentate ligand.

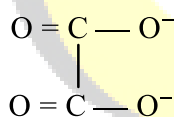
Symmetrical and unsymmetrical Bridging ligands:-

The bidentate ligands in which both the donor atoms are same are called symmetrical Bidentate ligand (AA) and in which both the donor atoms are different are called unsymmetrical bidentate ligand (AB)

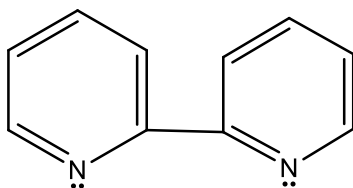
Symmetrical ligand



ethylenediamine (en)

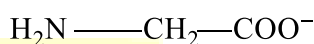


oxalato (ox)

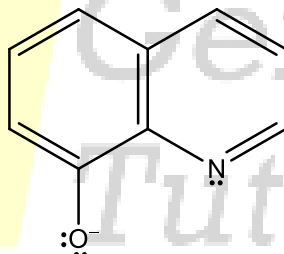


bipyridine (bpy)

unsymmetrical ligand



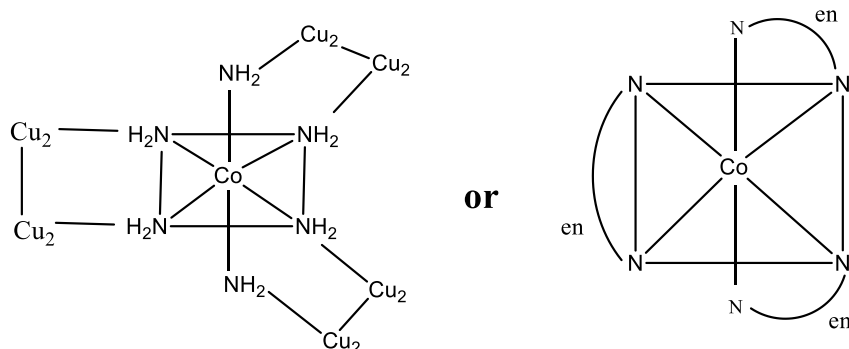
glycinato (gly)



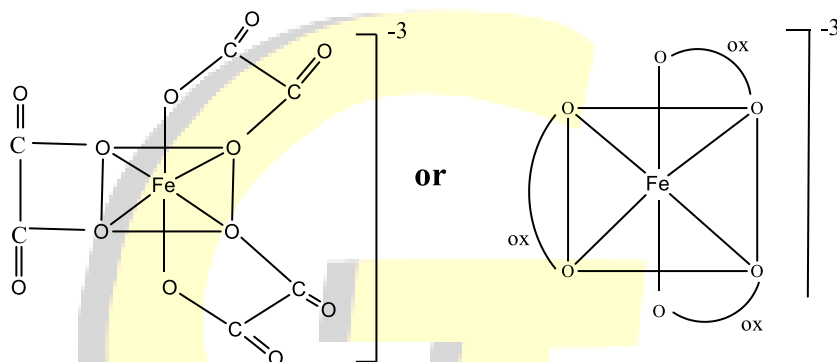
8-hydroxy quinolinato

* The attachment of symmetrical bidentate ligands to a metal cation can be represented by a curve $\overset{\text{A}}{\text{A}} \text{---} \text{L}$ where L is the abbreviation of symmetrical bidentate ligand & two A's are 2 similar donor atoms

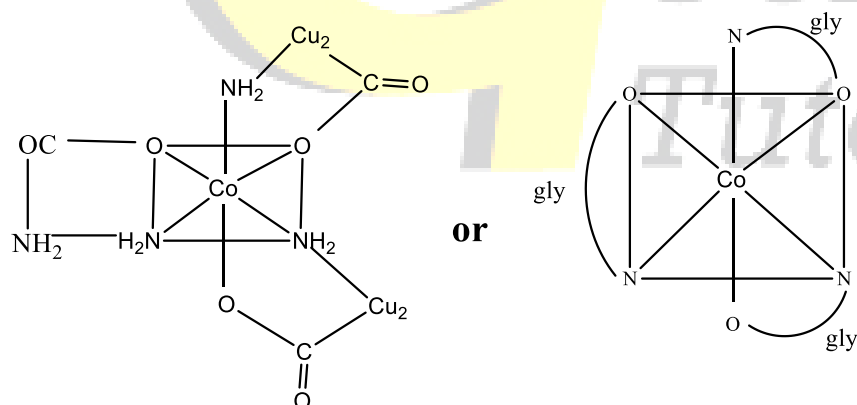
Ex.



Attachment of en to Co^{+3} in $[\text{Co}(\text{en})_3]^{+3}$ attachment of oxalate, $\text{C}_2\text{O}_4^{-2}$ ligand to Fe^{+3} ion:-



Attachment of unsymmetrical bidentate ligand ex. glycinato ($\text{NH}_2\text{CH}_2\text{COO}^-$ to Co^{+3})

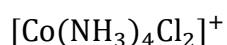


* Homoleptic and heteroleptic complexes

Complex in which a metal is bond to only one kind of donor atom/group

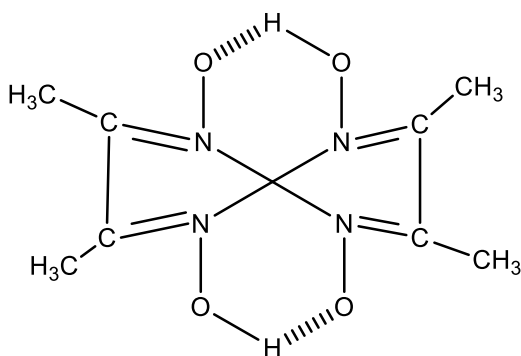
Ex. $[\text{Co}(\text{NH}_3)_6]^{+3}$

Complexes in which a metal is bond to more than one kind of donor atoms are called heteroleptic complexes



Ex. $[\text{Ni}(\text{Hdmg})_2]$

*** Dimethyl gloxime**



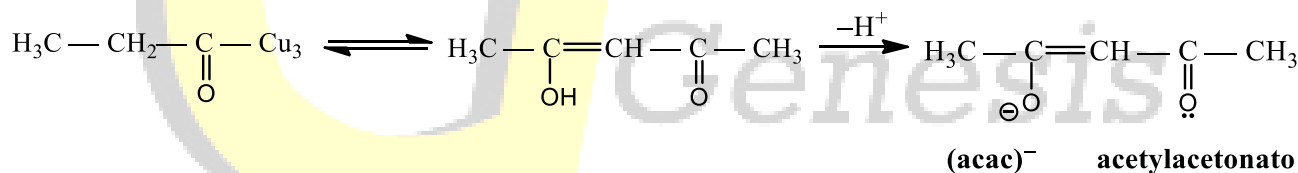
⇒ **Abbreviation for neutral form is dmgh₂ and dmgh for anionic form** where H stands for hydrogen

It is used in analysis of Pd or Ni

It is a dioxime derivation of diketone (butane 2, 3 dione)

Here a pair of dmgh⁻ ligands are joined through hydrogen bonds to give a macrocyclic ligands

*** Bidentate ligands:- (Acetyl acetone)**



Coordination number of a metal ion in its complexes is the number of donor atoms attached to it. Coordination number and geometry of the complexes are related to one another. For example, complexes with coordination number 4 are either tetrahedral or square planar and the complexes with coordination number 6 are octahedral. The coordination number and geometry of the complexes depend upon the following factors:

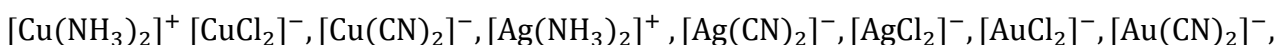
1. The size of metal ion or atom.
2. Size of the ligands and the steric interaction between the ligands.
3. Electronic interactions and the number of d-electrons in metal ion or atom
4. Whether the ligands form π -bonds with metal ion or not.

In general, the metal atom or ions of larger size (say 4d and 5d series transition metals and lanthanoids) favour the formation of complexes of higher coordination numbers because steric repulsion decreases with increase in size of central metal cation. For similar reasons, bulky ligands often form complexes of low coordination numbers and the smaller size ligands form complexes of higher coordination number. Complexes of higher coordination numbers are formed for the central metal cation or atom of 4d- and 5d- transition elements which lie on the left of the period and has a few number of d-electrons. The metal cation or atom having a small number of d-electrons can accept more electron pairs from the ligands, one example is $[\text{Mo}(\text{CN})_8]^{4-}$. On the other hand, the metal cations which lie on the right of the period and are rich in d-electrons form complexes of low coordination numbers. A few examples are $[\text{PtCl}_4]^{2-}$, $[\text{PdCl}_4]^{2-}$, $[\text{AgCl}_2]^-$ etc. These atoms or ions can accept less number of electrons from the ligands. Complexes of low coordination numbers are also formed when the ligands formed multiple bonds with metal cation, such as MnO_4^- , CrO_4^{2-} , $[\text{Ni}(\text{CO})_4]$ etc. The formation of multiple bonds between metal cation and ligands opposes the addition of more number of ligands.

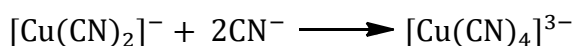
The coordination number of metal ions ranges from 1, as in ion pairs such as $\text{Na}^+ \text{Cl}^-$ in the gaseous state to 12 as in $(\text{Ce}(\text{NO}_3)_6)^{2-}$ ion. In general, the coordination number of metals in complexes are found to be 2 to 9, out of which coordination number 2, 4 and 6 are most common.

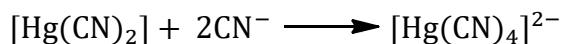
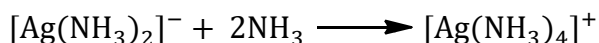
Coordination Number 2

A few number of complexes are known with coordination number 2. The complexes with coordination number 2 are given by Cu^+ , Ag^+ and Hg^{2+} ions (i.e., d^{10} species). These complexes have linear geometry. Some examples are

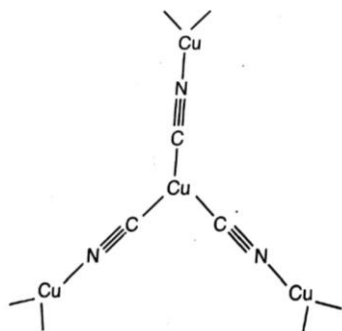


$[\text{Hg}(\text{CN})_2]$, $[\text{Hg}(\text{CH}_3)_2]$, $[\text{Au}(\text{PR}_3)_2]^+$ etc. These complexes are typically unstable towards the further addition of ligands to form complexes of higher coordination number 3 or 4 such as





The cyano complexes Ag^+ and Au^+ with coordination number 2 are less stable as they exist as discrete bis (cyano) complexes. The solid $\text{K}[\text{Cu}(\text{CN})_2]$ contains a chain like structure in which coordination number of Cu^+ is 3.



Chain structure of $[\text{Cu}(\text{CN})_2]^-$ in solid form.

The complexes of coordination number 2 may also be formed by the sterically hindered (ie, bulky) ligands such as $[\text{N}(\text{SiPh}_3)_2]^-$, $[\text{N}(\text{SiMe}_3)_2]^-$, $[\text{N}(\text{SiMePh}_2)_2]^-$, etc. with the metal ions such as Mn^{2+} , Fe^{2+} , Co^{2+} and Ni^{2+} . One important example is $\text{Fe}[\text{N}(\text{SiPh}_3)_2]_2$.

Coordination Number 3

This coordination number is rare in complexes and the geometries corresponding to coordination number 3 are trigonal planar and trigonal pyramidal. Some famous examples are $\text{K}[\text{Cu}(\text{CN})_2]$, CsCuCl_3 , infinite single chain, HgI_3^- and the pyramidal SnCl_3^- .

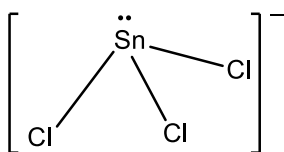


Figure 2.2 Trigonal pyramidal structure of SnCl_3^-

Coordination Number 4

This is the second most important coordination number in coordination chemistry after coordination number 6 which is to be discussed later. The geometry corresponding to the coordination number 4 is tetrahedral or square planar.

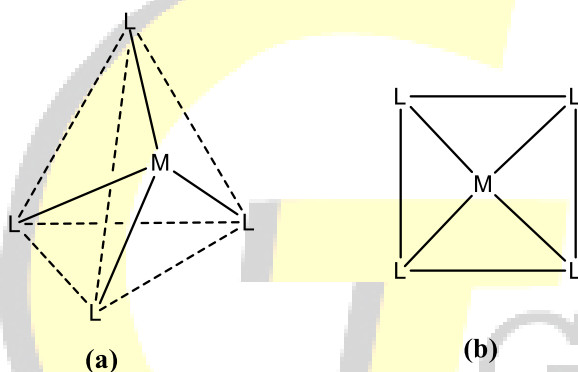
Tetrahedral complexes are favoured when the ligands like Cl^- , Br^- , I^- and the central metal cation or atom is smaller with (i) d^0 and d^{10} configuration and (ii) d^n configuration where square planar or octahedral is not favoured by number of d-electrons, such as

$\text{Fe}^{2+} (d^6), \text{Co}^{2+} (d^7), \text{Ni}^{2+} (d^8), \text{Cu}^{2+} (d^9)$ ions which form tetrahedral complexes with Cl^-, Br^- ions.

The oxoanions of transition metals in high oxidation states are, generally, tetrahedral such as $\text{VO}_4^{3-}, \text{CrO}_4^{2-}, \text{MnO}_4^-$ etc.

Square planar complexes are less favoured sterically than tetrahedral complexes. Therefore, these are prohibitively crowded by large ligands. as $\text{Co}^{2+} (3d^7), \text{Ni}^{2+} (3d^8)$ and $\text{Cu}^{2+} (3d^9)$ form square planar complexes with π - acceptor ligands such as CN^- . The metal ions belonging to 4d- and 5d- series transition elements such as $\text{Rh}^+, \text{Ir}^+, \text{Pd}^{2+}, \text{Pt}^{2+}, \text{Au}^{2+}$ form invariably square planar complexes regardless of the π -donor or π -acceptor character of the ligands. Examples of square planar complexes are:

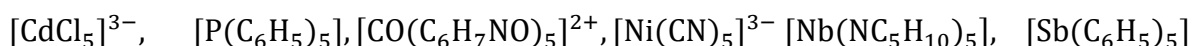
$[\text{Ni}(\text{CN})_4]^{2-}, [\text{Co}(\text{CN})_4]^{2-}, [\text{Cu}(\text{CN})_4]^{2-}, [\text{Ni}(\text{NH}_3)_4]^{2+}, [\text{PdCl}_4]^{2-}, [\text{PtCl}_4]^{2-}, [\text{AuCl}_4]^-$,
 $[\text{Rh}(\text{Me}_3\text{P})_3\text{Cl}], [\text{Ir}(\text{CO})(\text{Me}_3\text{P})_2\text{Cl}]$ etc.



(a) Tetrahedral (b) Square planar structure of complexes of Coordination Number 4

Coordination Number 5

The complexes of coordination number 5 are less common than that of coordination 4 and 6 for d-block element. The complexes corresponding to coordination number 5 are either square pyramidal (SP) or trigonal bipyramidal (TBP). However, both these geometries undergo some distortion from their ideal geometries. These two geometries often differ little in energy from one another. Muetterties and Guggenberger produced a series of coordination compounds of coordination number 5 to show a sharp transition of an ideal trigonal bipyramidal to square pyramidal

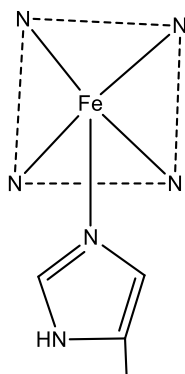


Trigonal bipyramidal

Intermediates (distorted)

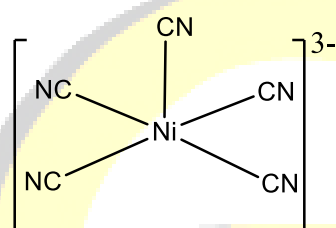
(square pyramidal)

In some cases it has been observed that the polydentate ligands or macrocyclic ligands favour the square pyramidal geometry. For example, the iron atom in deoxyhemoglobin and myoglobin has square pyramidal coordination.

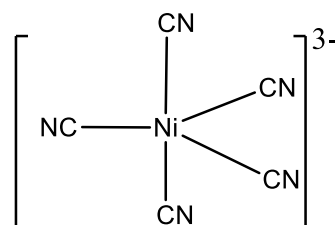


The five coordinated, Fe(II) deoxyhemoglobin

The $[\text{Ni}(\text{CN})_5]^{3-}$ ion can exist as both square pyramidal and trigonal bipyramidal [Figure] in the same crystal.

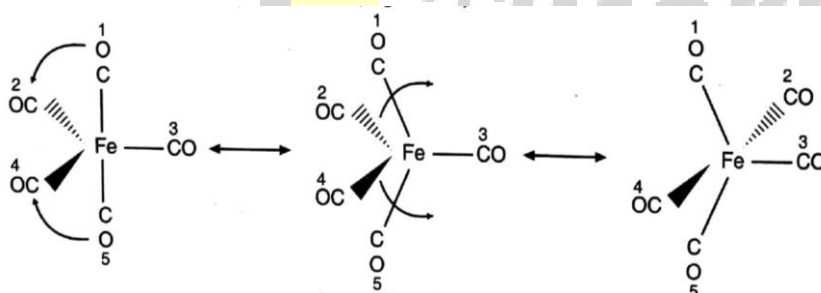


**(a) Square pyramidal geometry
of $[\text{Ni}(\text{CN})_5]^{3-}$**



**(b) Trigonal bipyramidal geometry
of $[\text{Ni}(\text{CN})_5]^{3-}$**

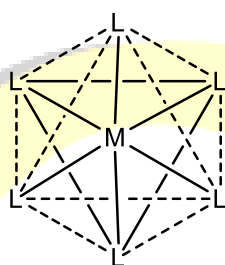
In general, trigonal bipyramidal with monodentate ligands are highly fluxional in solution, i.e. ligand that is equatorial at one moment becomes axial at the next moment. This change in position of ligands may occur by Berry pseudorotation



The $\text{Fe}(\text{CO})_5$ complex, for example, is trigonal bipyramidal in the crystal, however, in solution the axial and equatorial ligands exchange at a rate such that these ligands can not be distinguished by NMR which has a time scale $\sim 10^{-3}\text{s}$, and the ^{13}C nmr spectrum of $\text{Fe}(\text{CO})_5$ shows only one resonance. This indicates that the exchange of axial and equatorial ligands takes place at a rate that is fast on nmr scale. It is also observed that the exchange of these ligands is slow on IR time scale.

Coordination Number 6

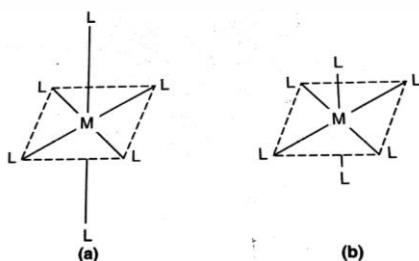
This is the most common and enormously important coordination number for transition metal complexes. The possible geometries corresponding to coordination number 6 may be hexagonal planar, trigonal prismatic, octahedral or tetragonally distorted octahedral. In a regular octahedral complex all the M–L bond distances are equal and the complexes have plane as well as centre of symmetries. In other words, we can say that the regular octahedral complexes are highly symmetric and have O_h symmetry. Examples of some regular octahedral complexes are: Complexes of Cr(III) like $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Cr}(\text{CN})_6]^{3-}$, complexes of Co(III) like $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Co}(\text{CN})_6]^{3-}$ complexes of Fe^{2+} like $[\text{Fe}(\text{CN})_6]^{4-}$, complexes of Ni^{2+} like $[\text{Ni}(\text{NH}_3)_6]^{2+}$ etc. The structure of regular octahedral complex, say ML_6 is shown in Figure.



The structure of regular octahedral complex

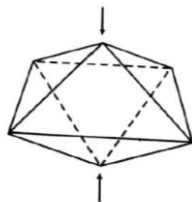
When different kind of ligands are present in an octahedral complex, the symmetry of the true octahedron can not be retained.

There are some complexes of coordination number 6 which have all the six ligands same but undergo some sort of distortion due to the electronic effect. The first is the tetragonal distortion, either elongation or compression along one of the fourfold rotational axes of the octahedral (Figure). This type of distortion has been discussed in Jahn-Teller distortion or Jahn-Teller effect.



Tetragonal distortion (a) Tetragonal elongation (b) Tetragonal compression

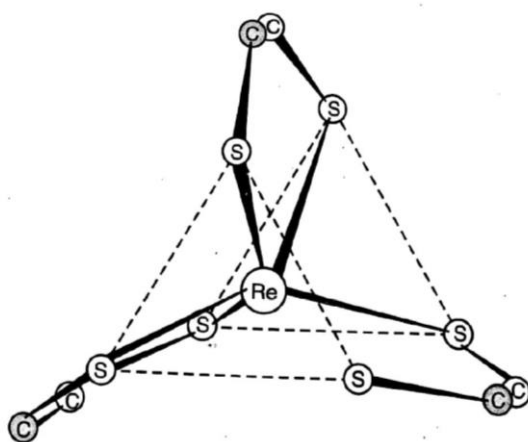
Another type of distortion is the elongation or compression, called trigonal distortion along one of the four threefold rotational axes of the octahedron which pass through the centres of the faces resulting in a trigonal antiprism.



Trigonal distortion

If the ligands of a regular octahedral complex like $[\text{Co}(\text{NH}_3)_6]^{3+}$ are replaced by chelating ligands like ethylenediamine $\text{NH}_2 - \text{CH}_2 - \text{CH}_2 - \text{NH}_2$ to form $[\text{Co}(\text{en})_3]^{3+}$, the symmetry of the regular octahedron is reduced from O_h to D_3 but it is not a real distortion.

The complexes having trigonal prismatic geometry (figure) are rare, but have been found in crystal lattices of sulphides of heavy metals for example MoS_2 and WS_2 . Trigonal prismatic complexes of d^0 configuration such as $[\text{Zr}(\text{CH}_3)_6]^{2-}$ and $[\text{W}(\text{CH}_3)_6]$ have also been isolated. The trigonal prismatic structure of $[\text{Re}(\text{S}_2\text{C}_2\text{Ph}_2)_3]$ is shown in figure.



Trigonal prismatic structure of $[\text{Re}(\text{S}_2\text{C}_2\text{Ph}_2)_3]$

Higher Coordination numbers

Coordination number 7 is not common. However it is encountered for a few 3d and some 4d and 5d metal complexes. Where the larger central metal ion can accommodate more than six ligands, geometries corresponding to the coordination number 7 are pentagonal bipyramidal, a capped octahedron and a capped trigonal prism (These three geometries are shown in Figure). In capped octahedron and capped trigonal prism, one ligand (the seventh ligand) occupies one of the eight faces.

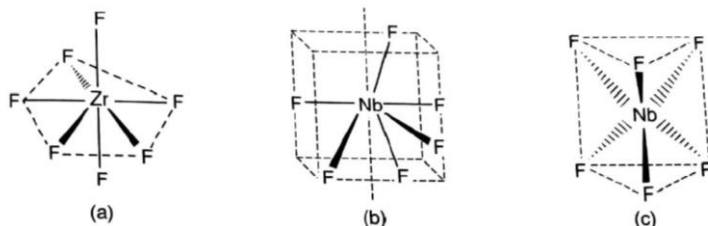
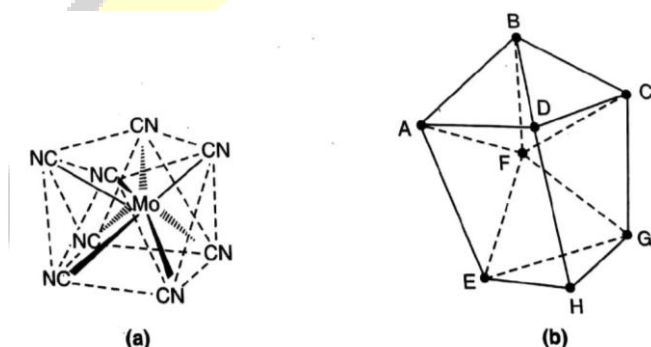


Figure (a) Pentagonal bipyramidal (b) Capped octahedron and (c) Capped trigonal prism

Some examples of complexes of coordination number 7 are $[\text{ZrF}_7]^{3-}$, $[\text{Mo}(\text{CNR})_7]^{2+}$, $[\text{ReOCl}_6]^{2-}$ and $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$

Coordination Number 8

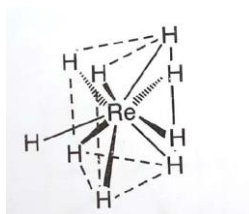
Coordination number 8 also can not be regarded as common. The possible geometries for complexes of coordination number 8 are square antiprismatic (Figure) and the trigonal dodecahedral (Figure). The two famous examples with their geometries are shown in figure



(a) Square antiprismatic and (b) Trigonal dodecahedral

Coordination Number 9

Coordination number 9 is shown by some *f*-block elements because of their larger size. Important examples are $[\text{Ln}(\text{H}_2\text{O})_9]^{2+}$, $[\text{Nd}(\text{H}_2\text{O})_9]^{3+}$. The examples of coordination number of 9 *d*-block elements are $[\text{TcH}_9]^{2-}$ and $[\text{ReH}_9]^{2-}$ is shown in figure



The structure of $[\text{ReH}_9]^{2-}$

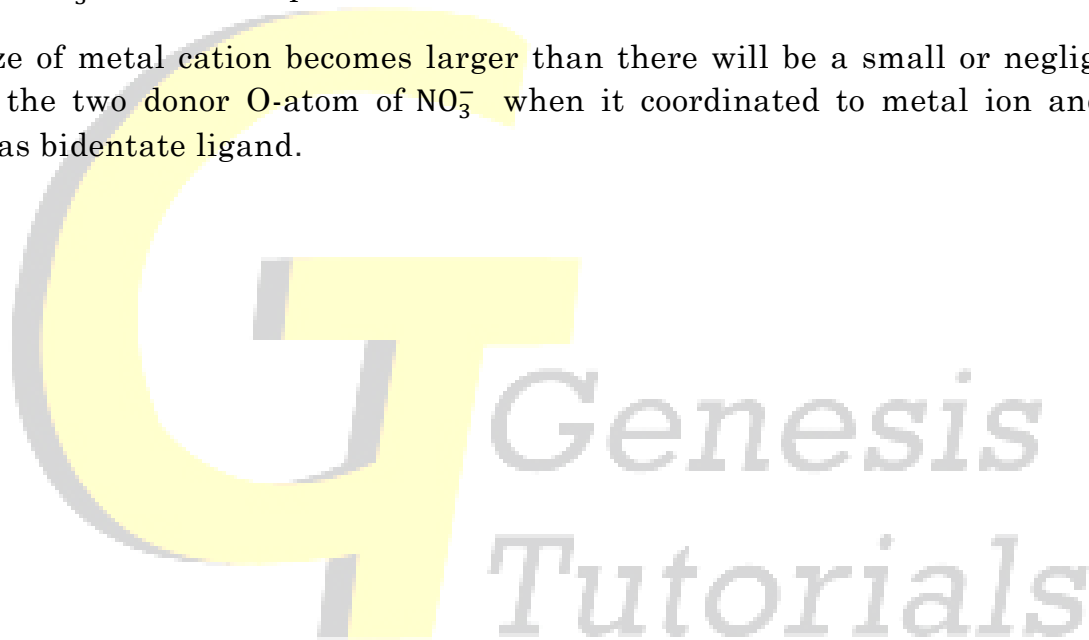
Coordination Number 10

Coordination number 10 is encountered in complexes of f-block M^{3+} ions. For example, $[Th(OX)_4(H_2O)_2]^{4-}$, Th has coordination number of 10. The higher coordination numbers are rare with d-block M^{3+} ions because their smaller size may be responsible for the ligand-ligand repulsion when they approach the metal ion.

Coordination Number 12

Coordination number 12 is also encountered in complexes of the f-block M^{3+} ions. An important example is $[Ce(NO_3)_6]^{2-}$ in which each NO_3^- ligand behaves as bidentate ligand. If the size of a metal cation is small then NO_3^- behaves as monodentate ligand. If, for instance, it acts as bidentate ligand with smaller cation, there will be strain between two donor O-atoms of a NO_3^- and the complex becomes unstable.

If the size of metal cation becomes larger than there will be a small or negligible strain between the two donor O-atom of NO_3^- when it coordinated to metal ion and thus NO_3^- behaves as bidentate ligand.



Detection of complex formation

1. Most of the complexes will be colored except d^5 (weak-field) and d^{10} systems. Hence, when a solution of the ligand is added to a solution of a metal salt, there will be a change in the color of metal salt solution for example, when ammonia is added in excess to aqueous copper sulfate solution (blue), the color changes to deep blue indicating complexes formation. This is the simplest way of detecting complex formation.
2. UV-visible spectrum can be used to further support this. The λ_{max} of the ligand (if already absorbs) and the metal salt solution (if already colored) will be shifted.
3. When the complex is decomposed with concentrated nitric acid, the original color of the metal salt solution will be restored.
4. The original property of the metal ion will be lost during complex formation. For example aqueous solution of Fe^{3+} will give brown color with KCNS(aq) . However, a complex of Fe^{3+} will not answer this test.

How to confirm complex formation?

1. Elemental analyses — C, H, N, S analyses

The percentages of these elements are determined by Elemental analyser and matched with the calculated value for the proposed structure. If these two match, then the proposed structure of the complex is correct.

2. Molar conductance measurements will tell us whether the complex is neutral or charged and also tell whether it is a 1: 1, or 1:2 etc complex.
3. Magnetic susceptibility measurements will tell us the number of unpaired electrons in the complex, if it is paramagnetic, and hence, the oxidation state of the central metal ion.
4. The coordination of the ligand with the metal is confirmed by IR and for IR spectra. The IR spectrum of the ligand is compared with that of the complex and from the shift in values of the N-H, C=O, O-H etc. we can confirm which atom is coordinated to the metal ion.
5. Electronic spectrum (UV-vis) of the complex will give us the oxidation state of the central metal and the geometry of the complex.
6. EPR spectrum for a paramagnetic complex through its hyperfine splitting will give us the number of unpaired electrons in the central metal 'g' value will give us information about the distortion.

7. TG and DTA will tell u about the thermal stability of the Complex and also about the decomposition of the ligands.

From all these, we confirm the structure of the complex.

3. Coordination geometry

3.1. Coordination number

Examples: $\text{Cu}(\text{NH}_3)_2^+$, $\text{Au}(\text{CN})_2^-$, HgCl_2

These are linear and the ligand-metal-ligand bond angle is 180° ; Cl-Ag-Cl . These metal ions have d^{10} configuration in the ground state. Even though the metal-ligand bond may be considered to be formed due to the overlap of a σ -orbital of the ligands with sp -hybridized metal orbital, actually some d -orbital contribution is also there in the bond formation. These hybrid orbitals will have 50% p_z character along with a small amount of d_{z^2} character and the remaining will be 's' character

3.2 Coordination number 3

It is a rare coordination number. In many crystalline compounds, the stoichiometry may be MX_3 but the actual coordination number may be 3 greater than the ligands are extremely bulky, this coordination number exists. In some of the systems, even when the ligands are not bulky, coordination number 3 exists. Example: $\text{KCu}(\text{CN})_2$, $\text{Pt}(\text{PPh}_3)_3$ complexes. The metal atom and the ligands are directly connected to it. In such cases, they lie on the same plane.

(VBT) Valence Bond Theory

This theory was developed by Pauling

Assumption of VBT

1. The bond between metal and ligand is covalent and is formed by overlapping of metal hybrid orbitals and ligand orbitals.

2. The central metal ion makes available a number of empty orbitals which are equal to its coordination number.

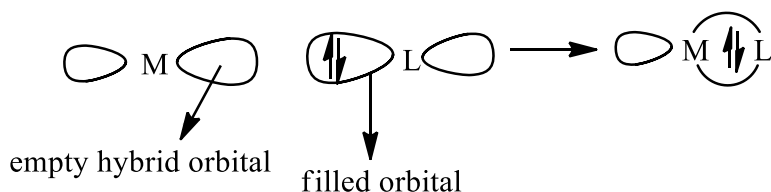
3. The vacant orbitals of central metal ion undergo hybridization as hybrid orbitals from strong and better overlapping than unhybridized orbitals. In hybridization, all orbitals can participate but they must not, vacant half-filled and fully-filled orbitals. More difference in the energies.

4. In VBT, hybridization was given more importance as transition metal orbitals of suitable energies 'd' mean atom have vacant hybridized and $(1-n)$ both orbitals participate. Complexes in which d orbitals are involved are called $(1-n)$ in which

inner orbital complexes and complexes in which nd orbitals are involved are called outer orbital complexes

Usually octahedral inner orbital complexes are more stable than those of octahedral outer orbital complexes

6. Thereafter the empty hybrid orbital of metal ion overlap with filled orbital of ligands to form covalent coordination bond

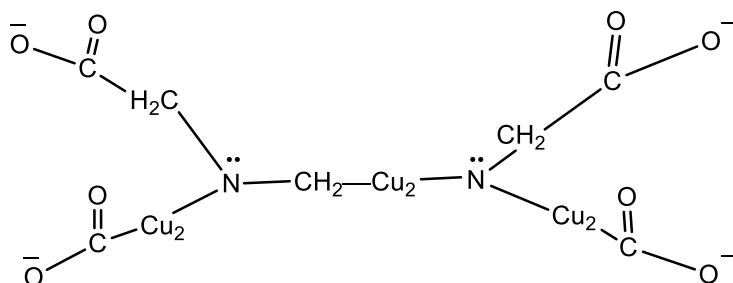


Magnetic moment and coordination number of central metal ion are important for deciding a geometry/hybridisation inner / outer nature of complex. The knowledge of magnetic moment gives idea about number of unpaired electrons $\mu = \sqrt{n(n+2)}$

8. According to Pauling ligands may be classified into two classes

- (a) **Strong ligands.** They have tendency to pair up the electrons of metal ion e.g., CO , CN^- etc.
- (b) **Weak ligands.** They do not have tendency to pair up the electrons of metal ion e.g., F^- , Br^- , H_2O etc. Therefore ligands will decide the type of hybridisation and magnetic moment of complex.

measured by the magnetic behaviour of compounds. The number of unpaired electrons determines which d orbitals are used. **Note**

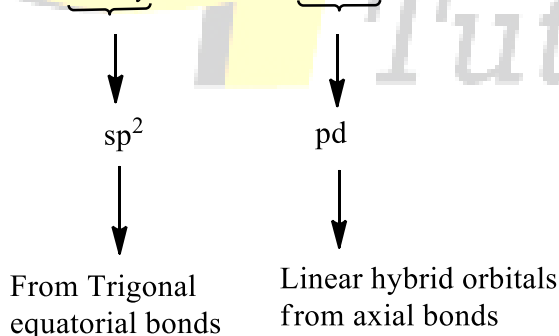


EDTA can form five rings by using 4 carboxylate groups and two amine nitrogens

Table: Hybrid orbital for common coordination geometries

C.N.	Hydri- b- idisation	Orbitals involved	Bond angle (s)	shape	example
2	sp	s and p_x	180°	linear	$[\text{Ag}(\text{NH}_3)_2]^+$
3	sp^2	s, p_x and p_y	120°	Triangular planar	BCl_3
4	sp^3	s, p_x , p_y & p_z	$109^\circ 28'$	Tetrahedral	$[\text{CoCl}_4]^{2-}$ $[\text{NiCl}_4]^{2-}$
4	sd^3	s, d_{xy} , d_{yz} , d_{zx}	$109^\circ 8'$	tetrahedral	MnO_4^- , $\text{Cr}_2\text{O}_7^{2-}$ CrO_7^{2-}
4	dsp^2 Or sp^2d	s, p_x , p_y , $d_{x^2-y^2}$ s, p_x , p_y , $d_{x^2-y^2}$	90° 90°	Square planar Square planar	$[\text{Ni}(\text{CN})_4]^{2-} (dsp^2)$ $[\text{Cu}(\text{NH}_3)_4]^{2+} (sp^2d)$
5	dsp^3	s, p_x , p_y , p_z & d_{z^2}	90° 120°	Trigonal pyramidal	$\text{Fe}(\text{CO})_5$
5	dsp^3	s, p_x , p_y , p_z & $d_{x^2-y^2}$	$>90^\circ$, $<$ 90°	Square pyramidal	$[\text{Ni}(\text{CN})_5]^{3-}$
6	d^2sp^3	4s, 4 p_x , 4 p_y , 4 p_z 3 $d_{x^2-y^2}$ & 3 d_{z^2}	90° , 90°	Inner orbital Octahedral	$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Fe}(\text{CN})_6]^{4-}$
6	sp^3d^2	4s, 4 p_x , 4 p_y , 4 p_z 4 $d_{x^2-y^2}$ & 4 d_{z^2}	90° , 90°	Outer orbital Octahedral	$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, $[\text{CoF}_6]^{4-}$

* $sp^3d \rightarrow$ combination of sp^2 hybrids and $p_z d_z^2$ hybrids



- (4) The non-bonding electrons of the metal ion/atom are rearranged in metal ion orbitals (e.g., pure s, p or d-orbitals as the case may be) which do not participate in forming the hybrid orbitals. Their arrangement of non bonding electrons takes place according to Hund's rules
- (5) The strong ligands have the tendency to push and pair up the nonbonding electrons present in the metal atomic orbitals whereas the weaker ligands have no such tendency. Pairing of electrons in metal atomic orbitals takes place according to Hund's rule.

In quantum mech. an atomic orbital is a mathematical function that describes the wave-like behaviour of either $1e^-$ or pair of e^- in atom

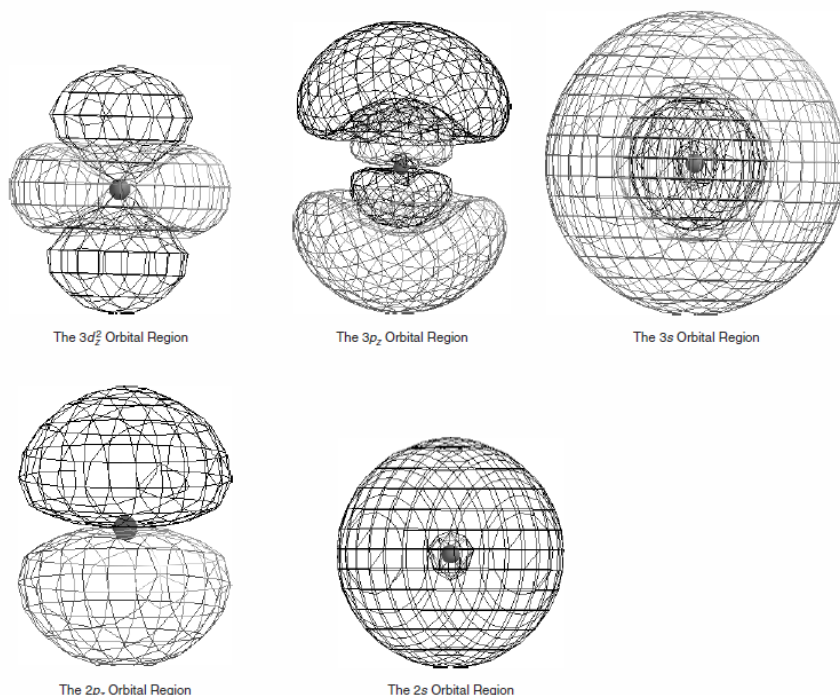
Orbital Regions

The *orbital region* is the region in space inside which the magnitude of an orbital function is larger than some specified small value. The magnitude of the orbital function has the same value on all parts of the boundary of the orbital region and this surface is sometimes called an *isosurface*. Since the square of the magnitude of the orbital function is the probability density, the orbital region is the region inside which the electron is most likely to be found. A common policy chooses a magnitude of the orbital at the boundary of the orbital regions such that 90% of the total probability of finding the electron lies inside the orbital region.

Any nodal surface divides the orbital region into discrete subregions, which we call *lobes*. It is usually possible to sketch an orbital region by first determining the nodal surfaces and then sketching lobes between the nodal surfaces. The wave function always has opposite signs in two lobes that are separated by a nodal surface, so it is not difficult to assign the sign for each lobe of a real orbital. Remember that any wave function can be multiplied by a constant, so that if we change all the signs of the lobes (multiplying by -1) no physical change is made.

Figure schematically depicts several orbital regions of real orbitals. The sign of the orbital function is indicated by showing one sign in color and the other in black. The orbital regions of complex orbitals differ from those of real orbitals. The magnitude of the complex exponential $e^{im\phi}$ or $e^{-im\phi}$ is equal to unity, so that the magnitude of the complex orbital does not depend on ϕ . We say that these orbital regions are *cylindrically symmetric*. The vertical nodal planes that occur in the real and imaginary parts do not occur in the probability density. The real orbitals have orbital regions with lobes that lie between their vertical nodal planes. The compactness of the lobes of the orbital regions of the real p and d functions often makes them more useful than the complex p and d orbitals in discussing chemical bonding.

A wave function with more nodes has a higher energy because it corresponds to a shorter de Broglie wavelength and a larger electron speed. With a particle in a onedimensional box, the number of nodes was (in addition to the nodes at the ends of the box) equal to $n - 1$, where n was the quantum number, and the energy was proportional to n^2 . With the harmonic oscillator, the number of nodes (in addition to the nodes at $|x| \rightarrow \infty$) was equal to v , the quantum number, and the energy was proportional to $v + 1/2$. In the hydrogen-like orbitals the number of nodal surfaces is equal to the quantum number n and the energy is proportional to $-1/n^2$.



Some orbital Regions of Hydrogen-Like orbitals. Positive region are black and negative region are in gray

Pictures of orbital regions are included in elementary chemistry and organic chemistry textbooks, but sometimes the distinction between the orbital and the orbital region is not emphasized. The orbital is a wave function, whereas the orbital region is a three-dimensional region in space, inside which the magnitude of the orbital function is larger than some specified small value.

PROBLEMS

The Orbitals of the Hydrogen-like Atom

- (a) Sketch the nodal surfaces for the first five energy eigenfunctions for a particle in a three-dimensional spherical box. *Hint:* The spherical harmonic functions are the same as with the hydrogen atom, and the pattern of nodes in the radial function is the same as with the hydrogen atom, except that the nodal sphere at infinity is replaced by a nodal sphere at the surface of the box.

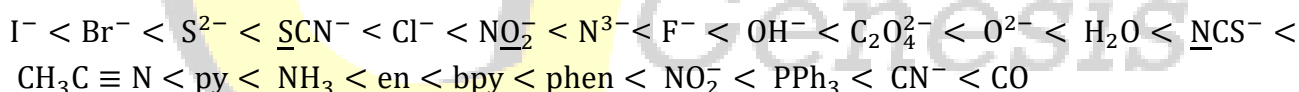
	Ions	Ligands Cl^-	H_2O	NH_3	en	CN^-
d^3	Cr^{3+}	13700	17400	21500	21900	26600
d^5	Mn^{2+}	7500	8500		10100	30000
	Fe^{3+}	11000	14300			(35000)
d^6	Fe^{2+}		10400			(32800)
	Co^{3+}		(20700)	(22900)	(23200)	(34800)
	Rh^{3+}	(20400)	(27000)	(34000)	(34600)	(45500)
d^8	Ni^{2+}	7500	8500	10800	11500	

Values are in cm^{-1} entries in parentheses are for low-spin complexes.

Source: H.B. Gray, *Electrons and chemical bonding*. Benjamin, Menlo Park (1965).

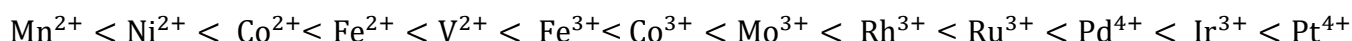
A note on good practice The convention in spectroscopic notation is to indicate transitions as [upper state] \leftarrow [lower state].

The ligand-field splitting parameter, Δ_o , varies systematically with the identity of the ligand. For instance, in the series of complexes $[\text{CoX}(\text{NH}_3)_5]^{n+}$ with $\text{X} = \text{I}^-, \text{Br}^-, \text{Cl}^-, \text{H}_2\text{O}$ and NH_3 , the colours range from purple (for $\text{X} = \text{I}^-$) through pink (for Cl^-) to yellow (with NH_3). This sequence indicates that the energy of the lowest energy electronic transition (and therefore Δ_o) increases as the ligands are varied along the series. The same order is followed regardless of the identity of the metal ion. Thus ligands can be arranged in a **spectrochemical series**, in which the members are arranged in order of increasing energy of transitions that occur when they are present in a complex:



(The donor atom in an ambidentate ligand is underlined.) Thus, the series indicates that, for the same metal, the optical absorption of the cyano complex will occur at higher energy than that of the corresponding chlorido complex. A ligand that gives rise to a high energy transition (such as CO) is referred to as a **strong-field ligand**, whereas one that gives rise to a low-energy transition (such as Br^-) is referred to as a **weak-field ligand**. Crystalfield theory alone cannot explain these strengths, but ligand-field theory can, as we shall see in Section 20.2.

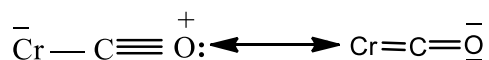
The ligand-field strength also depends on the identity of the central metal ion, the order being approximately:



The value of Δ_o , increases with increasing oxidation state of the central metal ion (compare the two entries for Fe and Co) and also increases down a group (compare, for instance, the locations of Co, Rh, and Ir). The variation with oxidation state reflects the smaller size of more highly charged ions and the consequently shorter metal-ligand distances and stronger interaction energies. The increase down a group reflects the larger size of the 4d and 5d orbitals compared with the compact 3d orbitals and the consequent stronger interactions with the ligands.

(b) Ligand-field stabilization energies

Key point:- The ground-state configuration of a complex reflects the relative values of the ligand-field splitting parameter and the pairing energy. For $3d^n$ species with $n = 4-7$, high-spin and low-spin complexes occur in the weak-field and strong-field cases, respectively. Complexes of 4d- and 5d-series metals are typically low-spin.



Bonding in Coordination compounds

There has been much work done in attempting to formulate theories to describe the bonding coordination compounds and to rationalize and predict their properties. The first success along these lines was the valence bond (VB) theory by **Linus Pauling** and other in the 1930s and following years. In the 1950s and 1960s the crystal field (CF) theory and its modifications, generally known under the label ligand field (LF) theory gained preeminence and in turn gradually gave way to the molecular orbital (MO) theory. Although both the valence bond and crystal field theories have been largely displaced as working models for the practicing inorganic chemistry, they continue to contribute to current discussions of coordination compounds.

Valence Bond Theory

From the valence bond point of view, formation of a complex involves reaction between **Lewis** bases (ligands) and a Lewis acid (metal or metal ion) with the formation of coordinate covalent (or dative) bonds between them. The model utilizes hybridization of metal s, p, and d valence orbitals to account for the observed structures and magnetic properties of complexes. For example, complexes of Pd(II) and Pt(II) are usually four coordinate, square planar and diamagnetic, and this arrangement is often found for Ni(II) complexes as well. Inasmuch as the free ion in the ground state in each case is paramagnetic ($d^8, ^3F$), the bonding picture has to include pairing of electrons as well as ligand-metal-ligand bond angles of 90° . Pauling suggested this occurs via hybridization of one $(n-1)d$, the ns, and two np orbitals to form four equivalent dsp^2 hybrids directed toward the corner of square. For example, in PtCl_4^{2-} the $5d_{x^2-y^2}$ orbital combines with 6s and $6p_x$ and $6p_y$ orbitals to form dsp^2 hybrid. These orbitals then participate in covalent σ bonds with the ligands, the bonding electron pairs being furnished by the ligands. The eight 5d electrons in the free ion are assigned as pairs to the four hybridized metal d orbitals.

With some ligands, such as Cl^- , Ni(II) four-coordinate complexes that are paramagnetic and tetrahedral. For these cases VB theory assumes the d orbital occupation of the complex to be the same as that of the free ion, which eliminates the possibility that valence-level d orbitals can accept electron pairs from the ligands. Hybrid orbitals of either the sp^3 or sd^3 type (involving $4p(p_x, p_y \text{ or } p_z)$ or $4d(d_{xz}, d_{yz}, d_{xy})$ orbitals or a combination of the two provide

the proper symmetry for the σ bonds as well as allowing for the magnetic properties due to two unpaired electrons. The examples presented here illustrate a useful rule originally called the "magnetic criterion of bond type" which allows prediction of the geometry of a four-coordinate d^8 complex if its magnetic properties are known: diamagnetic = square planar; paramagnetic = tetrahedral.

The valence bond picture for six-coordinate octahedral complexes involves d^2sp^3 hybridization of the metal. The specific d orbitals that meet the symmetry requirements for the metal-ligand σ bonds are the d_{z^2} and $d_{x^2-y^2}$. As with the four-coordinate d^8 complexes discussed above, the presence of unpaired electrons in some octahedral compounds renders the valence level $(n-1)d$ orbitals unavailable for bonding. This is true, for instance, for paramagnetic $[\text{CoF}_6]^{3-}$ the VB model invokes participation of 4s, 4p and 4d orbitals in the hybridization. However, for diamagnetic $[\text{Co}(\text{NH}_3)_6]^{3+}$ the $3d_{z^2}$ and $3d_{x^2-y^2}$ are vacant and participate in hybridization with 4s and 4p orbitals.

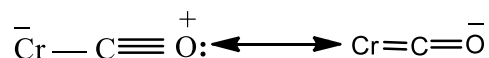
The Electroneutrality Principle and Back Bonding

One difficulty with the VB assumption of electron donation from ligands to metal ions is the buildup of formal negative charge on the metal. Since this is a problem that arises, in one form or another, in all complete treatments of coordination compounds, the following discussion is appropriate to all current bonding models.

Consider a complex of Co(II) such as $[\text{CoL}_6]^{2+}$. The six ligands share twelve electrons with the metal atom, thereby contributing to the formal charge on the metal a total of -6, which is only partially canceled by the metal's ionic charge of +2. From a formal charge point of view, the cobalt acquires a net-4 charge. However, Pauling pointed out why metals would not in fact exist with such unfavorable negative charges. Because donor atoms on ligands are in general highly electronegative (e.g., N, O, and the halogens), the bonding electrons will not be shared equally between the metal and ligands. Pauling suggested that complexes would be most stable when the electronegativity of the ligand was such that the metal achieved a condition of essentially zero net electrical charge. This tendency for zero or low electrical charges on atom rule-of-thumb known as the electroneutrality principle, and it is used to make predictions regarding electronic structure in many types of compounds, not only complexes. Pauling has made semi quantitative calculations correlating the stability of complexes with the charges on the central metal atom. For example it was shown that $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ and $[\text{Al}(\text{H}_2\text{O})_4]^{2+}$ are stable but $[\text{Be}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Be}(\text{NH}_3)_6]^{3+}$ are not. Four water molecules effectively neutralize the +2 ionic charge of beryllium, but six water molecules donate too much electron density.

There are many complexes in which the metal exists element of fairly low oxidation state and yet is bonded to an electronegativity. Among the most prominent examples are the transition metal carbonyls a large class of compounds in which the ligand (CO) is bound to the central metal through carbon. The source of stability in these complexes is the capacity

of the carbon monoxide ligand to accept a “back donation” of electron density from the metal atom. Within valence bond theory, this process can be described in terms of resonance:



To whatever extent canonical form II contributes to the resonance hybrid, electron density will be shifted from chromium to oxygen

Crystal Field Theory

The model that largely replaced valence bond theory for interpreting the chemistry of coordination compounds was the crystal field theory, first proposed in 1929 by **Hans Bethe**⁹. As originally conceived, it was a model based on a purely electrostatic interaction between the ligands and the metal ion. Subsequent modifications, which began as early as 1935 with papers by **J.H. Van Vleck**¹⁰ allow some covalence in the interaction. These adjusted versions of the original theory generally are called ligand field theory. It is an interesting feature of scientific history that, although the development of crystal and ligand field theories was contemporary with that of valence bond theory they remained largely within the province of solid state physics for about 20 years. Only in the 1950s did chemists begin to apply crystal field theory to transition metal complexes.

Pure crystal field theory assumes that the only interaction between the metal ion and the ligands is an electrostatic or ionic one with the ligands being regarded as negative point charges. Despite this rather unrealistic premise, the theory is quite successful in interpreting many important properties of complexes. Moreover, the symmetry considerations involved in the crystal field approach are identical to those of the molecular orbital method. The electrostatic model thus serves as a good introduction to modern theories of coordination chemistry.

In order to understand clearly the interactions that are responsible for crystal or ligand field effects in transition metal complexes, it is necessary to have a firm grasp of the geometrical relationship of the d orbitals. There is no unique way of representing the five d orbitals, but the most convenient representations are shown in figs 14.1 and 14.2 In fact, there are six wave functions that can be written for orbitals having.

Note:- (1) The Jahn teller theorem does not predict which type of distortion will takes place other than that the center of symmetry will remain.

(2) For a 'Zin' distortion, the splitting pattern is similar to that observed for a 'Z-out' but the energy ordering with the e_g and t_{2g} level is inverted

(3) Zout * Zin both tales place simultaneously, but then bonds will elongate or compress, how we will know??

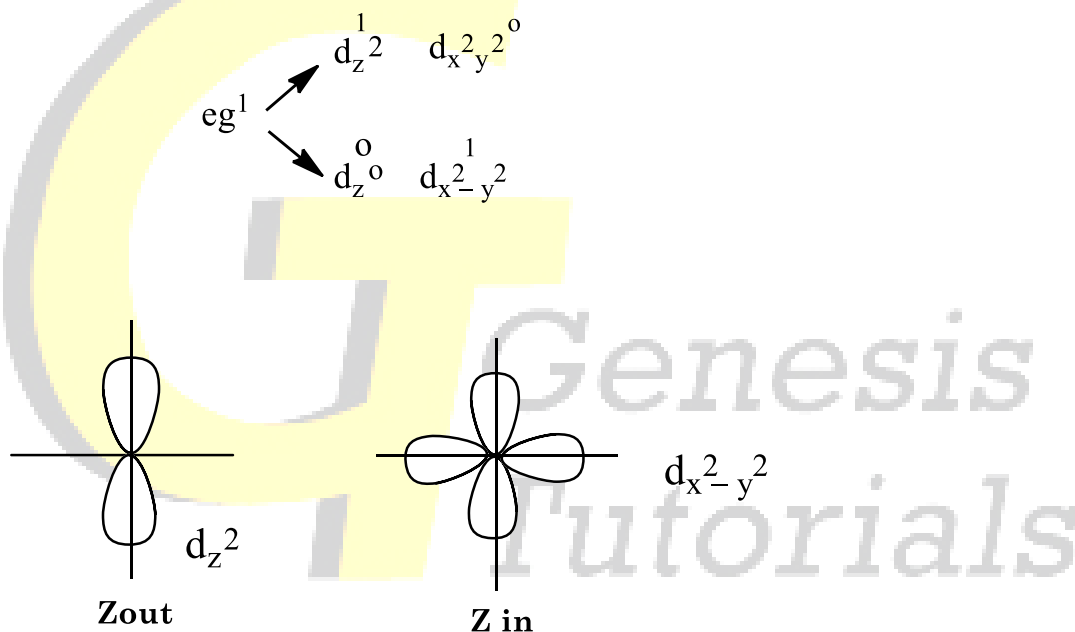
It Z-out dominates \rightarrow complex will be axially elongated

It Z-in dominates \rightarrow complex will be axially compressed

Question. When Z-in / Z out will dominate?

If e_g is unsymmetrical i.e e_g^1/e_g^3 then generally (Z out will dominate over Z in) how?

Ans:-

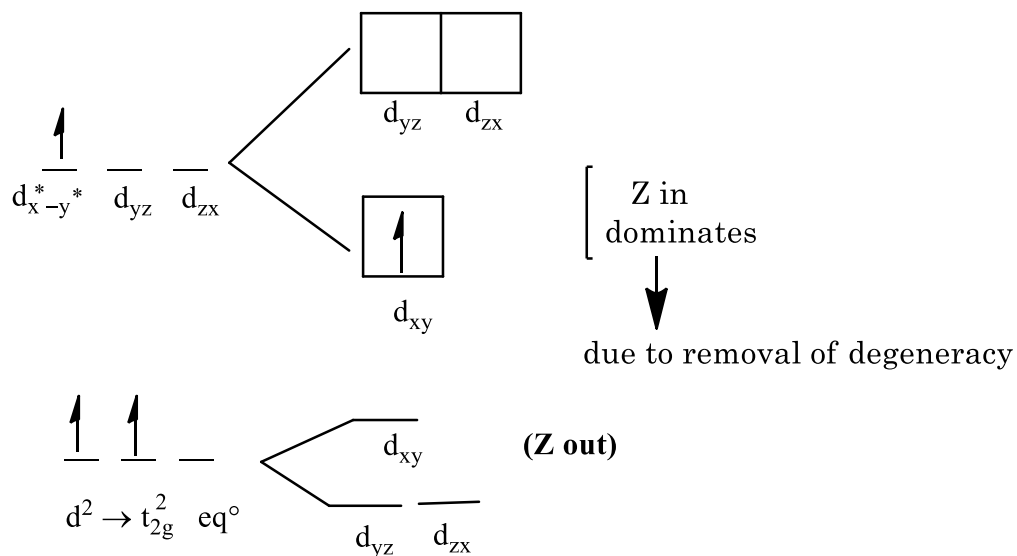


Here, in d_{z^2} , e^- density is only along one axis, while in $d_{x^2-y^2}$, e^- density is along 2 axis that means per lobe e^- density is less i.e. shielding will be less in case of $d_{x^2-y^2}$ so, ligands will tends to approach more in comparison to case when e^- density is more along Z-axis mean that when e^- is in d_{z^2} , ligands will be far and Z-out will dominate.

Note:- shielding (Z_{eff}) (ie. nuclear charge cover)

Shelding order:- $e_g > t_{2g}$

Now, cases of t_{2g} unsymmetrical:-



Note:-

eq^1 or eq^3	→	Z out dominates
t_{2g}^1 or t_{2g}^4	→	Z in dominates
t_{2g}^2 or t_{2g}^5	→	Z out dominates

Strength / Extent of Distortion:-

→ First we will see configuration in terms of t_{2g} & e_g

Note:- (e_g distortions are stronger than t_{2g} distortions)

Now, If configuration is same, then more e^- density, more will be distortion

$$eg^3 > eg^1$$

eg^3 → will be highly distorted

So,

Cu^{+2}
 Ag^{+2} So, JTD will increase on going down so 5d series oh complexes are highly distorted
 Au^{+2}

Hence, Au^{+2} is highly distorted among transition metal

Now, If we are taking same metal, but we are changing ligands so,

$$\text{distortion} \propto \text{field strength of ligand}$$

Ex.

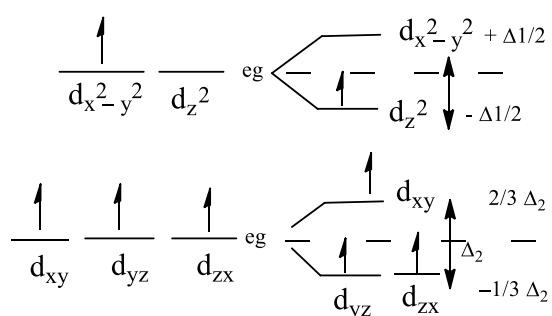
$[Ti(H_2O)_6]^{+2}$
 $[Fe(H_2O)_6]^{+2}$
 $[Cu(H_2O)_6]^{+2}$ which is highly distorted
 $[Au(H_2O)_6]^{+2}$

Note:- Due to JTD, internal symmetry comes (orbitals gain symmetry), but component, outer symmetry (geometry) becomes unsymmetry

Note:- JTD is also a type of splitting

JTSE:- John Teller stabilizing energy

For ex. → Z-out



so,

energy order:- $\Delta_0 \gg \Delta_1 > \Delta_2$

after splitting, if we consider the energy of all t_{2g} orbitals then $2\left(-\frac{1}{3}\Delta_2\right) + \frac{2}{3}\Delta_2 = 0$ (means in case of t_{2g} there is no net stabilisation)

but, if we see in case of eg^2 then d_{z^2} orbital will be stabilized $(-\frac{1}{2}\Delta_1)$

Note:- No pairing will be there because Δ_1 & Δ_2 energies are extremely small

Note:- Extra stabilization gained by the complex due to John Teller splitting or secondary splitting is called as John Teller stabilizing energy

→ It is always released energy i.e why complexes are Thermodynamically stabilized due to JTD.

The gain in thermodynamic stability is the reason for Removal of Degeneracy

So, $TOSE = CFSE + JTSE$

↓
Total stabilizing energy

(We, cannot calculate Δ_+ in terms of Δ_0 , but they are calculated experimentally)

Note:- oh complex in which CFSE is zero is

$\left[\begin{matrix} d^0 \\ d^5 \text{ (HS)} \\ d^{10} \end{matrix} \right]$ they are not field stabilized and they are also not JTD stable but vice versa is not true

i.e, those which do not contain JTD, will also not be CFSE stabilize (not true statement)

Except d^0, d^5, d^{10} in which JTD is zero

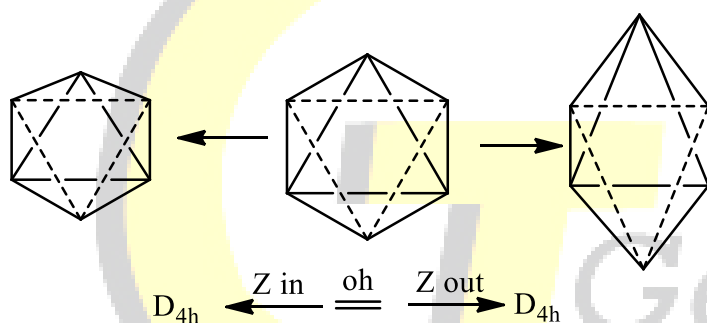
$\left[\begin{matrix} d^6 \text{ (LS)} \\ d^8 \\ d^3 \end{matrix} \right]$

Application of JTD

- (1) Effect on bond length and geometry
- (2) Thermodynamic stability of complex
- (3) Kinetic stability
- (4) Electronic Degeneracy removal
- (5) Non-existence of some complexes
- (6) Disproportionation reaction of $\text{Au}^{+2}(\text{oh})$
- (7) Explain the splitting of square planar complex.

(1) Effect on bond length and geometry

Geometry gets distorted from oh geometry



Ex. $d^9 \rightarrow$ axial bond elongates eq. bond compress

Ex. $d^1 \rightarrow$ axial bond compress eq. bond elongate

(2) Thermodynamic stability of complex

Increases due to JTD

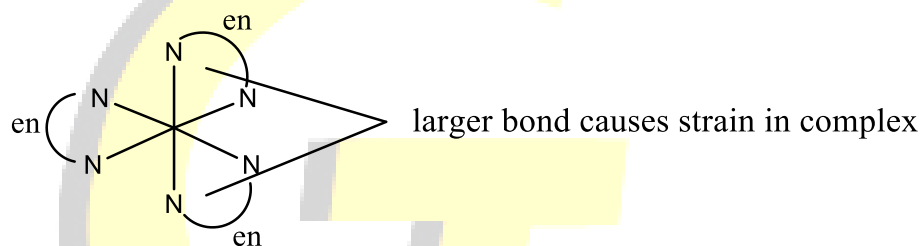
$$d^8 < d^9 < d^{10}$$

Cu^{+2} complexes are more stable than Ni^{+2} and Zn^{+2} complexes

Note:- Some of the strongest evidence for John Teller effect in TM compound comes from the structure studies of solid containing d^9 (Cu^{+2} ion)

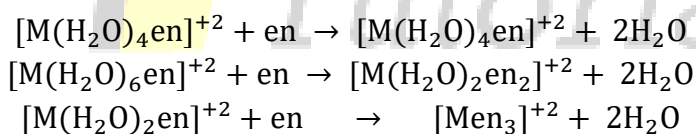
Distortion by either elongation or compression will leads to stabilization of Cu(II) complex. However experimentally measurements show that distortion is generally elongation along Z-axis

Note:- The nature of chelate rings tends to restrict the distortion of a complex from perfect oh, because JTD causes strain as seen in Cu complex of $[\text{Cu(en)}_3]^{+3}$



Ex. An example of conflict between stabilization from JT effect & chelate geometrical requirements is found in ethylene diamine complexes of Cu^{+2} .

$[\text{Cu(en)}_3]^{+2}$ is formed by stepwise replacement of water molecules.



Each step is associated with its equilibrium or stability constant, which measures the tendency for formation of mono, bis, tris (en) complex.

* The values of these constants for the ions Mn^{+2} to Zn^{+2} shows a uniform trend of gradually increase stability from left to right across the series (Irving William series)

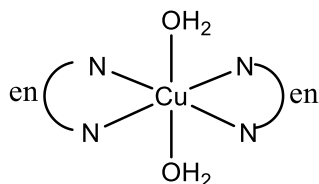
But Cu^{+2} ion is seen as a exception because $[\text{Cu(en)}_3]^{+2}$ is remarkably unstable

* Even the existence of this complex was questioned

* Here, the value of K_3 (a measure of the tendency to add a 3rd en ligand is the lowest of the ions in the series reaction though K_1 & K_2) values are highest

This lack of stability for this tris complex can be traced directly to the tendency of 6-coordinate d^9 ion to undergo distortion.

Now, $[M(en)_2H_2O]^{+2} \rightarrow$ bis (ethylene diamine) complex can distort readily by letting the two trans molecules to move out from the Cu, leaving 2 en rings relatively unchanged

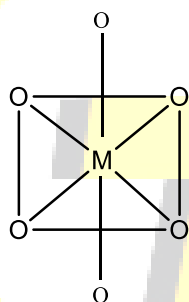


No strain (stable)

Besides this a number of chelated structure are known

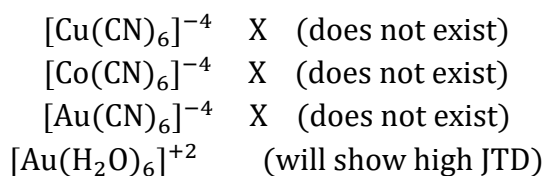
(3) Kinetic stability

Cu complex are highly thermodynamically stable & are kinetically reactive.



Due to JTD, axial bond elongates, bond becomes weak and can be easily substituted (i.e. will give substitution reaction easily)

Note:- strong ligand cause more distortion and axial bonds will be highly elongated & in absence of heating also two axial ligand will remove



$\frac{d^7}{d^9} \rightarrow$ with strong ligand oh complex does not occur due to JTD

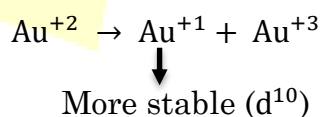
(4) Disproportionation reaction of Au^{+2} (oh)

Complexes of Au(II) ion are unstable and undergoes disproportionation to Au(I) & Au(III) whereas the complex of Cu(II) & Ag(II) are comparatively more stable

- * All have d^9 configuration & undergoes JTD. Since Δ value increase on moving down the group, therefore Δ value for Au(II) complexes is maximum among the three
- * The high Δ values causes a high destabilization of the last e^- in $d_{x^2-y^2}$ orbital and can be easily removed or transferred to other Au^{+2} ion due to which one Au becomes d^8 & other becomes d^{10} (self exchange of e^-)

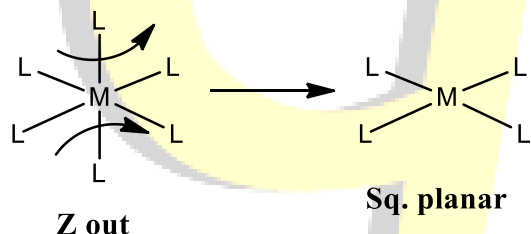
Hence, Au(II) becomes externally reactive & can undergoes either oxidation to Au(III) (d^8 system) or a reduction to Au(I) , d^{10} system.

Au(III) forms square planar complex while Au(I) forms a linear complex

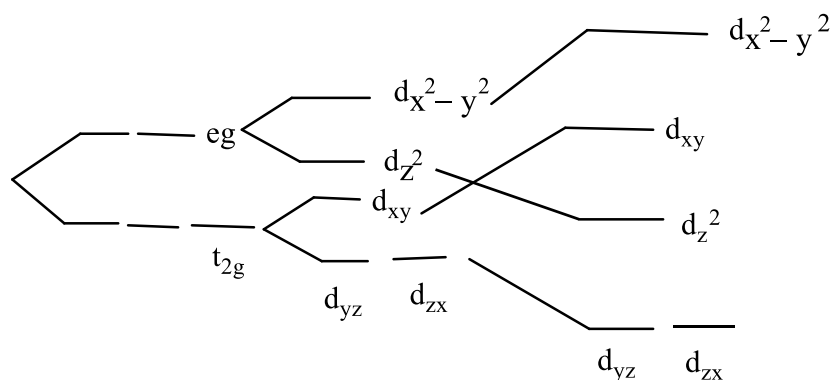


While Cu^{+2} complexes are more stable than Cu^{+1} complex.

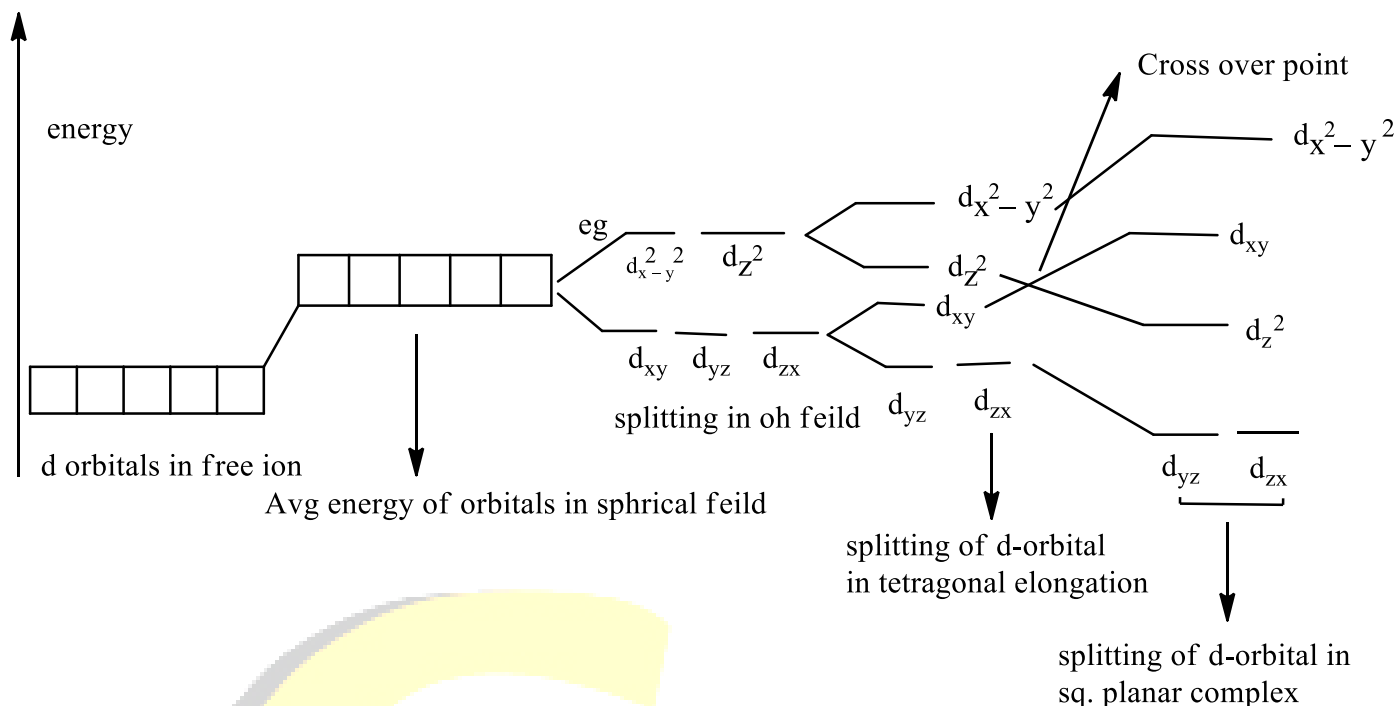
(5) Square planar as an extreme case of Z-out



Note:- eq orbital fast split splitting in 3d series



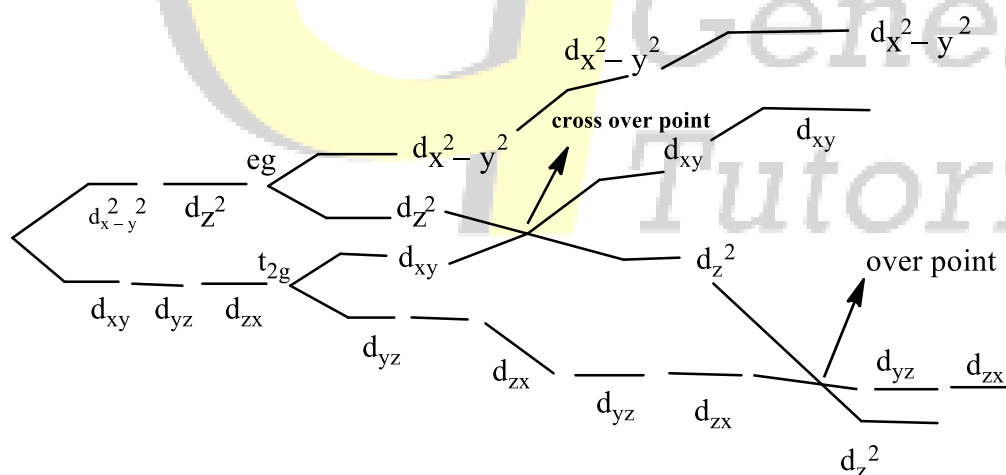
Or



Ex. $[\text{Ni}(\text{CN})_4]^{-2}$ ex. $[\text{Cu}(\text{NH}_3)_4]^{+2}$

Energy order:- $d_{x^2-y^2} > d_{xy} > d_{z^2} > (d_{zx} = d_{yz})$

Splitting in 4d/5d series

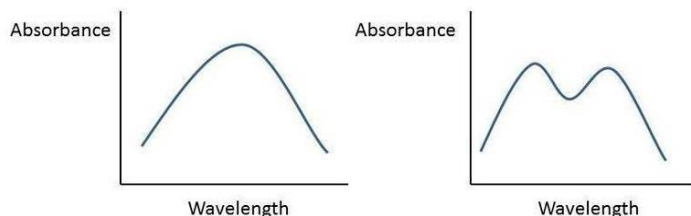


Energy order:- $d_{z^2} < d_{zx} = d_{yz} < d_{xy} < d_{x^2-y^2}$

Question. In which of the splitting dig. Cross over & overtake both occurs?

- (a) $[\text{Ni}(\text{CN})_4]^{-2}$
- (b) $[\text{Ni}(\text{en})_2]^{+2}$
- (c) $[\text{Pt}(\text{CN})_4]^{-2}$
- (d) $[\text{NiCl}_4]^{-2}$

* **Spectroscopy:** - (1) JTD can be observed by using a variety of spectroscopic techniques. UV-vis absorption spectroscopy technique UV-Vis absorption spectroscopy distortion causes splitting of bands in the spectrum due to reduction in symmetry (oh to D_4h), hence due to JTD number of bands increase.



Static and dynamic (JTD)

Static JTD complexes showing tetragonal distortion under all condition i.e in solid as well in solution either at lower or relatively higher temperature. This distortion is called static JTD, hence complexes with measureable bond length difference are example of static JTD behaviors

But there are some exceptions to the John Teller distortion in which certain physical properties corresponds to symmetric structures when distortions are expected.

In these complexes no distortion can be detected at room temperature because the direction of distortion randomly moves among the available symmetry axes of the complexes more rapidly then the physical measurement. This is called Dynamic JTD.

Thus the physical measurement detects an average structure with or weak distortion

* The distortions can be detected at freezing temperature because cooling of the compound will show the oscillation enough resulting in a single distorted structure.

Ex. $[\text{Cu}(\text{NO}_2)_6]^{-4}$, exhibit full range of static & dynamic john Teller effects

Static and dynamic (JTD)

Dynamic JTD:- Compound showing same bond lengths at normal condition, (RT) but different bond lengths at low temperature called dynamic JTD, due to fluxionating it is not observed at room temperature

Ex $[\text{Ti}(\text{H}_2\text{O})_6]^{+2}$

At room temperature

Normal bond length $-27^\circ\text{C} <$ shows two types of bond length

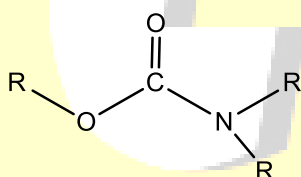
Static JTD:- Compound which shows distortions at normal condition- i.e. different bond length, at room temperature is called static JTD. (at high temperature can show 1 peak)

$[\text{Cu}(\text{H}_2\text{O})_6]^{+2}$, at 25°C

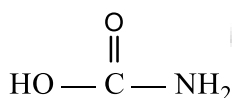
Axial bonds $>$ bond length

At 100°C all bond lengths are same but it does not mean it is dynamic

Note:- carbamate



Derived from carbonic acid



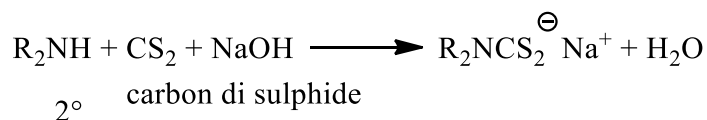
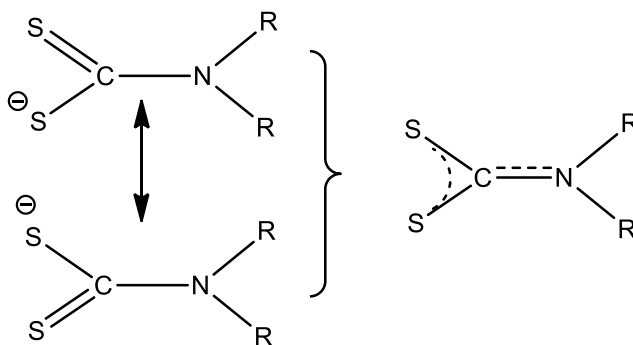
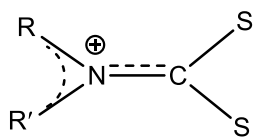
Di thio carbonate \rightarrow is a functional group in organic chemistry

It is the analog of a carbonate in which both oxygen atoms are replaced by Sulphur atoms (when oxygen atom is replaced \rightarrow thio carbonate)

Ex. Sodium diethyl di thio carbonate Na^+

Are used in vulcanization of rubber

R → ethyl



**Genesis
Tutorials**